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CHEMISTRY OF PLANETARY ATMOSPHERES AND COMETS

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*Because of consolidation of research grants this report covers an odd period of time. Work on NASA grant NGR-33-018-016, now consolidated with NsG-261, is brought up to date in this report.

CHEMISTRY OF PLANETARY ATMOSPHERES AND COMETS

Microwave Emission Studies

The emission of microwave radiation from glow discharges through SO_2 and CO_2 but not through noble gases, air, etc. has been observed and previously reported to NASA. This work has now been extended in an effort to understand better the nature of the emission. The emission has been found to be very pressure dependent with the optimum pressure for emission being less than 100 microns for CO_2 and SO_2 in a noise generator system. Examining the emission with an oscilloscope it was found that emission occurred in short pulses rather than being continuous . Because of the nature of the circuitry of our receiver such pulses appear as a semi-continuous meter reading when the receiver is operated in the " peak" mode. Each pulse was very energetic, $\sim 10^{-8}$ watts for SO_2, but the duration was only about 2 microseconds. About 10 or more of these were emitted per second from SO_2 in the noise generator system. When a larger volume was surveyed by use of tapered waveguide transitions, many more pulses could be observed per unit time. With CO_2 the emission was of a similar character except that each pulse was much less energetic. The mechanism leading to emission is not known at present, but it does not seem that it can be the same as that leading to the commonly observed emission from rare gas discharges which corresponds to the electron temperature. The phenomenon is of interest not only because of its application to the Venus atmosphere but also from a basic scientific viewpoint and should probably be investigated further. A detailed discussion with

NASA personnel with regard to future work in this area is planned.

CO + O-atom Reaction

Research into the mechanism of this reaction is continuing. Results to date indicate that the reaction is two-body with a very low heat of activation. The evaluation of the results is being considered in light of an unexpected oxidation process recently observed. The addition of small amounts of NO_2 directly into the reaction vessel results in a much greater carbon dioxide formation. This could be explained by a simple excited molecule mechanism except that it is not consistent with the known combustion kinetics of the CO flame. Since the original measurements of the O-atom concentration were made with an NO_2 titration technique some correction to the observed CO_2 product may be necessary. However, the reaction time in the previous experiments was much shorter as the NO_2 was added just upstream of the mass spectrometer. Possibly other results presented in the literature by other investigators may have to be re-evaluated in this light since NO and NO_2 are common impurities.

Photochemistry with Bromine Lamp

Previously reported photochemical studies of the oxygen-ozone and carbon dioxide systems have now either been published or are in press. More recently irradiations of methane and methane-ammonia mixtures have been carried out. The NH_3 dissociates to form N_2 and H_2 but little effect is observed with the methane. The presence of small amounts of higher hydrocarbons as impurities in the methane has complicated the observations and efforts are now underway to remove this source of interference.

Nitrogen Atom Recombination Studies

The recombination of N-atoms at low pressures has been studied using the same apparatus previously used for investigation of reactions of O-atoms with NO and SO. The light emitting reaction was found to be second order at lower pressures and approximately 2.5 order at the higher pressures studied. An inverse predissociation mechanism is believed to be the cause of this emission. Investigations of the band spectra at various pressures in the 10-30 micron region are now in progress.

The suggestion of an inverse predissociation process in the nitrogen atom recombination raises many objections as was evident from the discussion at the Durham meeting. Although none of the objections appears to have a sound basis, it was deemed worthwhile to be sure of the data obtained and, if possible, to add additional supporting evidence as, for example, from spectroscopic studies. The additional work to date does substantiate the earlier results and it is expected that a publication will be forthcoming soon.

Radical Resonance Radiation

The measurement of radical concentrations by a resonance technique has been initiated using the OH radical for the first experiments. In this method radiation from OH radicals in the 3064 A region is obtained by passing water and argon through an alternating discharge. The emission can then be concentrated on a low pressure flame or reaction zone and any OH radicals present may absorb the incident radiation and re-emit it as resonance radiation. The system is shown schematically in Figure 1. The

photomultiplier with oscilloscope readout observes a cross-section of the incident beam. The intensity of the observed re-emission is a measure of the OH concentration in the reaction zone. Flame reactions in general emit light but this is a steady emission. The resonance emission is an alternating signal since the original incident light (at 3064 A) is produced by an alternating discharge and the two emissions may be readily distinguished.

A number of difficulties may arise but the initial experiments have been quite successful. Figures 2 and 3 show the reacting gas emitting light, Figure 2 in the visible and Figure 3 in the ultraviolet. Figures 4 and 5 show the same gases with the incident beam on. The column of light is due to the resonance of the OH bands. Photographically a quartz lens was used with appropriate filters and the light in Figures 3, 4, and 5 is due solely to the 3064 A OH band system, OH ($A^2\,\Sigma^+ \rightarrow X^2\Pi$). The decrease in intensity of the resonance light column from Figure 4 to Figure 5 represents a decrease in OH radical concentration.

We feel that this technique is applicable in many areas of experimental reaction kinetics and will be an important analytical tool. A preliminary report will be submitted to a journal in the near future.

Presentations and Publications

"The Chemiluminescent NO-O-atom Reaction" by D. Applebaum, P. Harteck, and R.R. Reeves has been published in Photochemistry and Photobiology 4, 1003 (1965).

" The Bromine Ultraviolet Lamp: Studies of the Oxygen-Ozone and Carbon Dioxide Equilibria" by B.A. Thompson, R.R. Reeves, Jr., and P. Harteck has been published in the Journal of Physical Chemistry 69, 3964 (1965).

" Photodetachment of Molecules, Radicals, and Atoms from Surfaces by Ultraviolet Radiation" by R.R. Reeves, P. Harteck, and E.W. Albers was presented at the Symposium on Interstellar Grains at RPI, August 1965. Preparation of this paper in final form for publication is nearly complete and copies should be sent to NASA shortly.

" Radiation Equilibria Pertinent to Planetary Atmospheres" by P. Harteck, R.R. Reeves, Jr., B.A. Thompson, and R.W. Waldron, presented at the CACR Symposium in Visby, Sweden in August 1965, has been submitted for publication in Tellus. Copies have been sent to NASA.

" Photochemical Equilibrium Studies of Carbon Dioxide and Their Significance for the Venus Atmosphere" by R.R. Reeves, Jr., P. Harteck, B. A. Thompson, and R.W. Waldron, presented at the ACS meeting in Atlantic City, N.J., September 1965, has been accepted for publication in the Journal of Physical Chemistry. Copies have been sent to NASA.

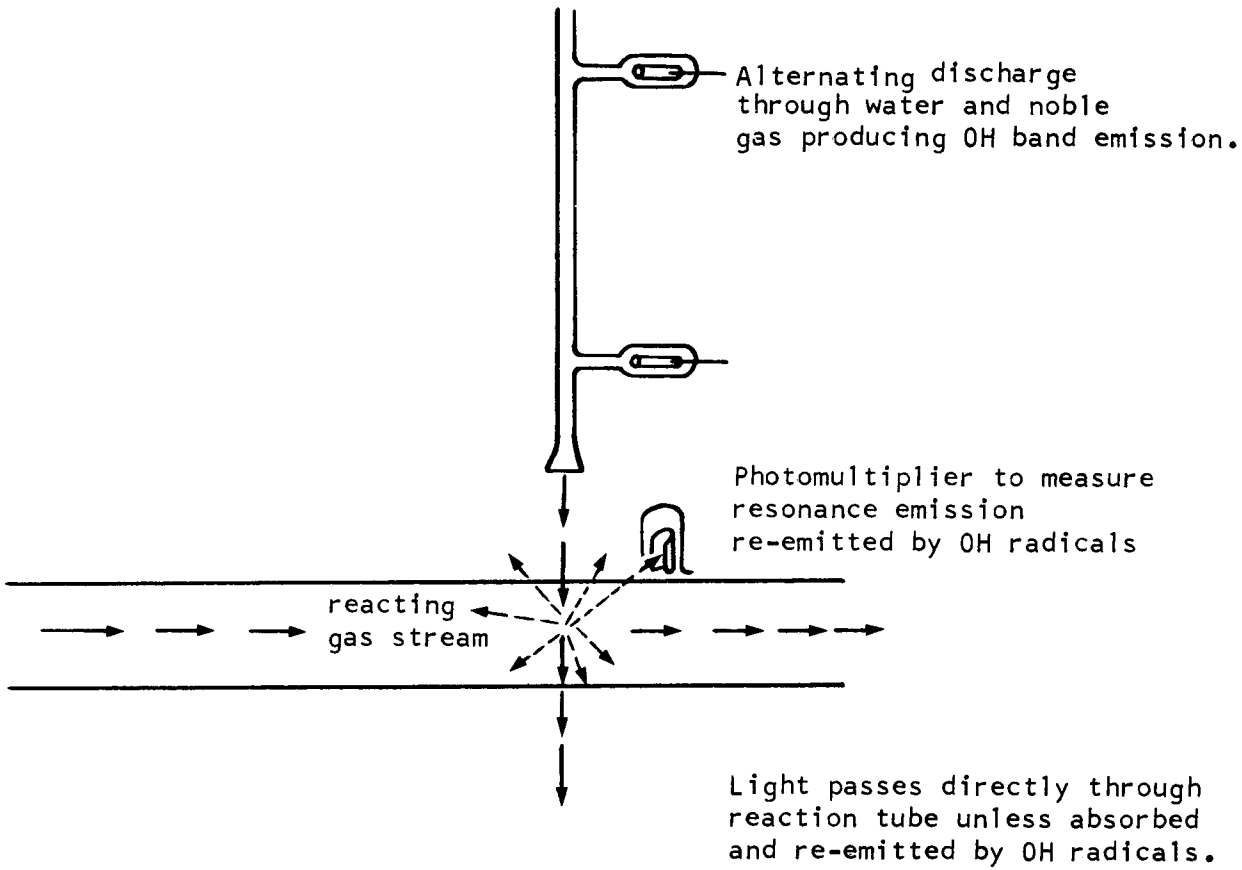

Figure 1

OH Radical Resonance Radiation

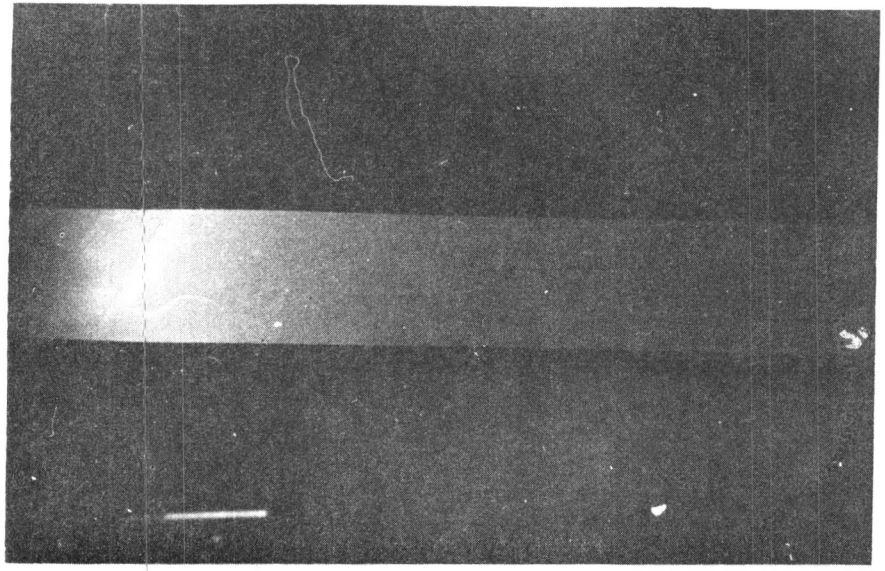

Figure 2

Emission is observed in the visible region from the reaction of NO_2 with H-atoms. Oxygen atoms and nitric oxide produced result in the emission in this region. As an intermediate OH radicals are formed.

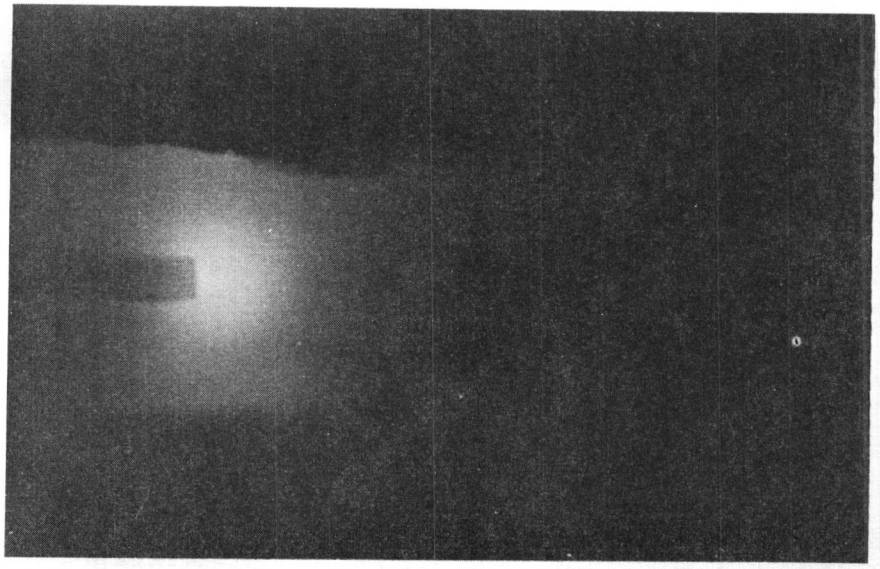

Figure 3

A close-up of the reaction system of figure 2. An ultraviolet filter was used to eliminate visible light and only emission from the OH $A^2\Sigma \rightarrow X^2\Pi$ bands (3064 A system) is observed. Note the difference in the distribution of light emission in the visible region (Figure 2), and ultraviolet region (band emission) shown in this figure.

Figure 4

Identical conditions as in figure 3, except for the addition of an incident beam, of OH radical emission ($OH A^2\Sigma^+ \rightarrow OH\ X^2\Pi$), which appeared as a thin vertical column due to resonance radiation from the OH radicals present in the reacting gas stream.

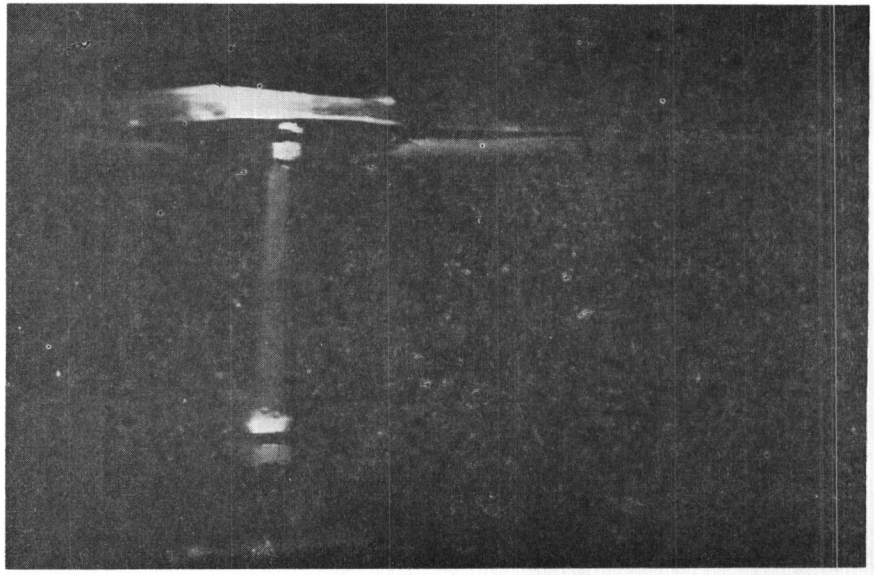

Figure 5

The OH emission from the flame itself was reduced by varying the flow conditions. The OH resonance radiation was still readily observed.